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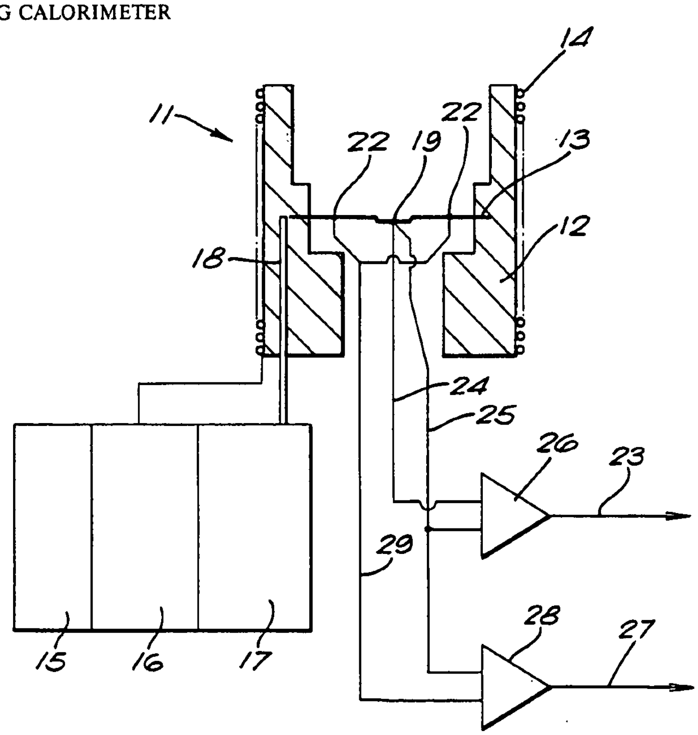
(54) Title: DIFFERENTIAL SCANNING CALORIMETER

(57) Abstract

A differential scanning calorimeter in the form of a furnace (11) including a sensor plate (13) within a furnace wall (12). The sensor plate (13) includes a single central sample location (19). There is a temperature sensor (21) beneath the sample location and secondary temperature sensors (22) radially located between the sample location (19) and the furnace wall (12). In use, a sample on the sample location (19) is submitted to a temperature regime; its temperature is monitored and compared with the temperature determined by the secondary temperature sensors (22).



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## DIFFERENTIAL SCANNING CALORIMETER

The present invention relates to differential scanning calorimeters.

A differential scanning calorimeter (DSC) is an instrument used in the thermal analysis of samples. The essence of the technique employed is to subject the sample to a temperature regime and to measure the temperature of the sample in response to the temperature regime. The regime may include lowering the temperature of the sample, raising the temperature of the sample or keeping the temperature steady (or a combination of these), all over a period of time.

The technique is carried out using a small furnace whose temperature can be precisely controlled. In practice, in existing systems, a reference material is used at the same time as the sample and temperature measurements are taken of both materials using thermocouples. The reference material is a stable inert material which has a flat response over the relevant temperature range. The derived energy signal that results in the case of the sample is caused by the energy required for the sample to undergo physical changes (transitions) e.g. solid - liquid - gas phase changes. The reference material, being inert, will not undergo any transitions and will therefore give a reasonably true representation of the thermal profile of the environment. The sample, however, will have absorbed or released energy when undergoing a phase change and this will be manifested as a minute increase or decrease in the sample temperature. As the reference has only absorbed the temperature profile of the environment, no temperature changes, apart from the imposed environment profile, will

be registered and so a differential signal will be generated between the sample thermocouple and the reference thermocouple. This signal can provide sample heat capacity data and when a transition occurs the level of heat capacity will change. In the case of a melt, a peak will be observed on the graph output trace and the area beneath the peak is proportional to the latent heat of fusion for that material. Other transitions occur which cause a shift in heat capacity, e.g. a Glass Transition in a polymer or rubber.

Unfortunately, monitoring the reference temperature via a reference material causes degradation of the signal and ultimately reduced resolution due to thermal noise being imposed on the signal. The noise is generated through a high thermal resistance being present between the material and the thermocouple junction, in the form of the sample/crucible, crucible/sensor plate, sensor plate/thermocouple interfaces which represent a complex 3 layer interface of differing materials that are subject to physical movements during heating. In conventional systems, this arrangement occurs twice, once for the sample and once for the reference material. This signal quality is again compromised due to the fact that the conventional twin crucible cell unit is totally thermally asymmetric. One side of each crucible, and thus the sample, is closer to the heat source than the other. This causes signal degradation due to sample/reference "cross-talk".

It is also known to incorporate some weight measuring device to measure the weight of the sample. By combining this information with the temperature data, it is possible to perform a thermogravimetric analysis (TGA) to determine various thermal properties associated with the sample.

According to the invention, there is provided a differential scanning calorimeter in the form of a furnace including a sensor plate and a furnace wall, the sensor plate including a single generally centrally placed sample location, the plate including a temperature sensor at the sample location and secondary radially displaced temperature sensors generally located between the furnace wall and the sample location; the calorimeter including means for accurately maintaining and varying the temperature of the furnace and means for comparing the temperature sensed by the sensor at the sample with the temperature determined by the secondary temperature sensors.

Thus, in the present invention, a single central location for the sample is employed. No reference material is used at all. In a preferred embodiment, a thermocouple is located immediately beneath the sample and four (or more) secondary thermocouples are radially distributed around the sample location. In this system, temperature measurements are taken by the thermocouple immediately beneath the sample and also by the secondary thermocouples. The sample temperatures are compared with those of the secondary thermocouples. The difference will be made up of any temperature gradient between the sample and secondary thermocouples and also any anomalies caused by inherent properties of the sample material at the particular temperature in question. Such anomalies would be caused, for example, by a phase change or a chemical reaction.

The absence of a reference material effectively makes the device self-referencing. It has the basic advantage that an entirely symmetric heat distribution throughout the furnace and plate is in fact not as critical as in known systems since the temperature of the

sample is compared with what is effectively an average radial plate temperature. This temperature difference is a measure of the total heat flow into or out of the sample thermocouple.

Thus, the system of the present invention addresses the problems of the prior art by dispensing with a reference material and its crucible, by locating the sample and its crucible in the centre of the sensor plate which is the equilibrium point of heat flow. In addition, the reference/sample thermocouple configuration gives a measure of total system heat flow into or out of the sensor plate. By dispensing with the need for a reference crucible and reference material, the signal to noise ratio is improved since interfacial thermal noise is now only generated at the sample location. A further improvement in signal quality is realised by the inherent thermal symmetry. Heat transfer between the sample crucible and the plate is radially symmetrical since all points on the crucible periphery are the same distance from the furnace wall.

Unlike a conventional DSC which measures a differential heat flow between the sample and a reference and is, therefore, highly susceptible to furnace/plate thermal symmetries, the system according to the invention measures total heat flow and is thus capable of considerably better baseline reproducibility.

In one form of the invention, the furnace wall may be of pure (99.99%) silver. This provides an efficient thermal path to the sensor plate. The sensor plate may be of a nimonic alloy, such as Chromel (T.M).

In a preferred embodiment, the sensor plate is a silicon wafer. Silicon is a very stable material and exhibits no thermal transitions between -170 and 1000°C It has a similar tensile strength to steel and is

chemically inert. A silicon base may therefore provide a much more stable instrument response. Enhanced chemical resistance can readily be imparted to the wafer by surface nitridation or some similar surface treatment. Thermocouple junctions can be formed on the wafer surface by vapour deposition, or similar treatment of the appropriate alloys as tracks. Track overlays can then produce the thermocouple junctions. These can also be protected by a special chemically resistant layer. Since the sample junction can be on the sample side of the wafer, improved sensitivity can be realised.

Preferably, the entire furnace is composed of silicon. Silicon is less costly than silver and the fact that the plate and wall are made of the same material avoids any difficulties with differential expansions with temperature. The use of silicon in this way may also improve data quality by removing noise generated by differential plate/furnace expansion. The furnace could then also be chemically hardened for extended usage. Furthermore, the temperature range of the instrument would be extended to 1000°C. Conventional materials for a "low temperature" DSC permit operation to a maximum of 700°C.

A silicon wafer base also lends itself to the incorporation of a weighing device. One way in which this can be achieved is to cut a "platform" from the silicon wafer at the sample location. The platform is resiliently attached to the surrounding silicon wafer with a result that any sample placed on the platform will cause it to be displaced. The displacement will be proportional to the weight and is reproducible with temperature. Minute variations caused by sample weight changes can be detected using laser interferometry or laser beam deflection. A low-cost medium resolution

balance may be provided by employing the Whetstone-bridge technology that is currently used in sophisticated pressure transducers. The silicon wafer can be ion implanted or similarly processed to construct thermocouples directly onto the surface in the same manner that the Bridge circuitry is constructed for pressure transducers. By forming the weight sensor as part of the DSC itself, simultaneous weight and calorimetric measurements will be possible.

To obtain DSC measurements at temperatures beyond 1000°C, the plate and furnace wall may be constructed of high performance ceramics and/or metals or alloys. Higher temperature thermocouples may be deposited, as described for silicon, or bonded directly to the plate.

For higher temperature TGA measurements, the silicon weight sensor or wafer, may be remotely positioned from the hot zone of the furnace. The sample holder may be attached to the wafer sensor by rigid "stalk". A thermocouple situated beneath the sample may be connected to tracks deposited on the wafer and from there the signal may be connected to suitable electronics via lead out wires. Simultaneous DSC-TGA could employ a similar system to that described for TGA above. The sample support may be a sensor plate situated in the furnace hot zone but not touching the furnace. Thermocouples may be connected as described for TGA. In such higher temperature systems, the furnace/plate or furnace/plate/wafer sensor assembly can be hermetically sealed to ensure good atmosphere control.

To obtain DSC measurements at temperatures beyond 1000°C, the plate and furnace wall may be constructed of high performance ceramics and/or metals or alloys. Higher temperature thermocouples may be deposited, as described for silicon, or bonded directly to the plate.

These materials may also, of course be used for low temperature applications. Furthermore, these materials may be used in the same way as silicon for measuring sample weight changes for TGA and simultaneous DSC-TGA.

Modulation of the heat reaching the sample permit the measurement of properties such as thermal conductivity and the reversibility and kinetics of transitions, by monitoring the amplitude and distortion of the original modulation waveform measured by the sample thermocouple, for such an operation it is desirable to "frequency-map" the transitions detected, that is to say, for taking measurements at a number of frequencies to derive the kinetic data.

One technique for modulating the heat reaching the sample is to impose a waveform on the current conducted by the furnace windings. However, this applied modulation frequency is limited by the thermal inertia of the furnace/sensor plate assembly, but still permits some frequency mapping. Alternatively, a pulse or pulses of heat can be generated at the sample thermocouple by passing a current through it. In this configuration the thermocouple is called a Peltier junction and can be switched rapidly from heat source to heat sensor. More flexibility is offered by using a pulsed laser to administer heat pulses directly or indirectly to the sample. Since silicon is transparent to infra red radiation, it is envisaged that an infra red laser could access the sample through the furnace or lid.

Pulsed or modulated heating can also be employed by placing a thermocouple in contact with the sample top surface. Thermal gradients, and therefore thermal conductivity between this and the plate, can then be measured. Heat can be applied as a single pulse or pulse train upwards or downwards through the sample. One

[redacted]



thermocouple/Peltier junction may be used as a source of heat and the other to measure temperature. These can be alternated if desired. A laser can also be used to apply controlled pulses to the sample top surface.

The differential scanning calorimeter of the invention therefore enables more sensitive and accurate measurements of a material's thermal properties to be taken, and with greater ease. The parameters measured are phase change and chemical reaction enthalpies and heat capacity, as in conventional DSC. In addition to improving basic data quality, additional measurements such as thermal conductivity and transition reversibility are facilitated.

The preferred materials used for the construction of the device will permit the integration of a weight sensing element enabling simultaneous calorimetry and TGA in a very compact unit.

Figure 1 is a simplified part-cutaway perspective view of a furnace forming part of a calorimeter in accordance with the invention;

Figure 2 is a schematic vertical section through a calorimeter in accordance with the invention; and

Figure 3 is a schematic vertical section through a calorimeter additionally adapted for high temperature thermogravimetric analysis.

Figures 1 and 2 shows a furnace 11 for a self-referencing differential calorimeter. The furnace 11 comprises a wall 12 of silver and a base or heat sensor disc 13 of Chromel (T.M.). The wall 12 is heated by means of an external heater coil 14. The heating cycle is achieved by means of a power supply 15, a furnace programmer 16 a furnace controller 17 and a control thermocouple 18 embedded in the wall 12.

The disc 13 has at its centre crucible location

point 19 for the sample. Beneath the sample point 19 there is a sample thermocouple 21, and at four symmetrical radially spaced locations in the disc 13 there are respective reference thermocouples 22 (though, there could of course be more, or even as few as three or two). A sample temperature signal 23 is generated by the sample thermocouple 21 via leads 24 and 25 and via an amplifier 26. A differential temperature signal 27 is computed in an amplifier 28 from signals from the sample thermocouple 21 and the reference thermocouples 22 via leads 29 and 25.

In use, the operational temperature range would be typically -170°C to 700°C though this could be extended up to 1000°C by the use of silicon for the wall 12 and plate 13. Lower temperatures could be attained by using liquid nitrogen or helium in a cooling jacket (not shown). Also, water or compressed air could be used in conjunction with the cooling jacket to cool the furnace rapidly.

Typical heating rates might be 0.1 to 100k/min. Cooling rates could be much more rapid if quenching were employed e.g. 1000k/min. A pressure range of about 1000kg/mm$^2$ down to below ambient is envisaged.

Figure 3 an alternative embodiment adapted additionally for high temperature TGA. The calorimeter 31 includes a zirconia wall 32 which acts as a heat sink, and a silicon wafer or ceramic base 33. Again, there is a central sample location 35. The calorimeter 11 is located within a housing comprising three ceramic walls. A carbon heater element 34 is located on the outer surface of the inner wall 36, and a vacuum chamber 37 is formed between the inner and intermediate walls 36,38. The outer wall 39 is spaced from the intermediate wall 38. The top and bottom are closed off by a lid 41 and

floor 42, respectively.

The calorimeter 31 is supported by a rod 43 which passes through the floor 42 via a frictionless support system such as air bearings. The rod 42 is itself supported from a silicon wafer 44 which is spaced from the floor 42, the intervening space optionally being filled with a thermal insulator (not shown).

In use, the displacement of the silicon wafer 44 is proportional to the weight of the sample and minute changes in displacement would represent changes in sample weight. The displacement is measured by means of a laser interferometer or by similar technology (not shown). By using a silicon wafer sensor "pad" in this way, sample weight can be measured with a maximum estimated limit of 1.0 gramme. Resolution of weight measurement would be down to 0.1 microgramme.

**CLAIMS**

1. A differential scanning calorimeter in the form of a furnace (11) including a sensor plate (13) and a furnace wall(12), the sensor plate (13) including a single generally centrally placed sample location (19), the plate (13) including a temperature sensor (21) at the sample location (19) and secondary temperature sensors (22) radially located between the sample location (19) and the furnace wall (12); the calorimeter (11) including means (14-18) for accurately maintaining and varying the temperature of the furnace (11) and means for comparing the temperature sensed by the sensor (21) at the sample with the temperature determined by the secondary temperature sensors (22).

2. A calorimeter as claimed in Claim 1, characterised in that the sensor plate (13) is a silicon wafer.

3. A calorimeter as claimed in Claim 1 or Claim 2, characterised in that the furnace wall (12) is of silicon.

4. A calorimeter as claimed in Claim 1, characterised in that the furnace wall (12) is of silver and/or the sensor plate (13) is of a nimonic alloy.

5. A calorimeter as claimed in Claim 1, characterised in that the furnace wall (12) and/or the sensor plate (13) are of a ceramic material.

6. A calorimeter as claimed in any preceding Claim, characterised in that a weighing device, the weighing device comprising a member (44) resiliently supporting

the sensor plate (33) and means for determining the displacement of the member (44) in response to the weight a sample located on the sensor plate (33).

7. A calorimeter as claimed in Claim 6, characterised in that the sensor plate (33) is located within a heat sink (32) which is supported by the member (44) via an elongate rod (43).

8. A calorimeter as claimed in Claim 7, characterised in that the heat sink (32) is of zirconia.

9. A method of performing a thermal analysis of a material which comprises: locating a sample of the material within a calorimeter; subjecting the sample to a temperature regime; measuring the temperature of the sample in response to the temperature regime; characterised by simultaneously measuring the temperature at other locations within the calorimeter to determine a calorimeter temperature, comparing this with the sample temperature and analysing the difference between the calorimeter temperature and the sample temperature during the temperature regime.

10. A method as claimed in Claim 9, characterised by additionally determining changes in the weight of the sample.

11. A method as claimed in Claim 10, characterised in that the changes in the weight of the sample are detected by supporting the sample from a resilient member and monitoring changes in the position of the member during the temperature regime.

FIG. 1

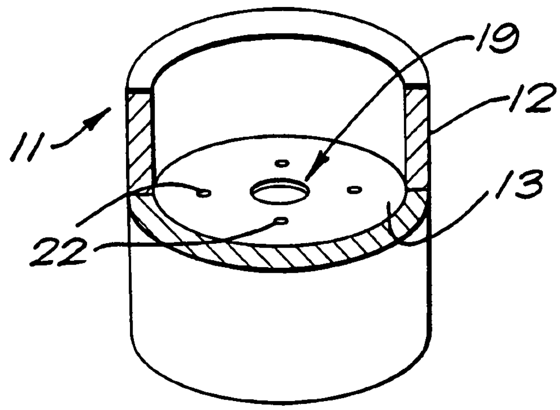


FIG. 3

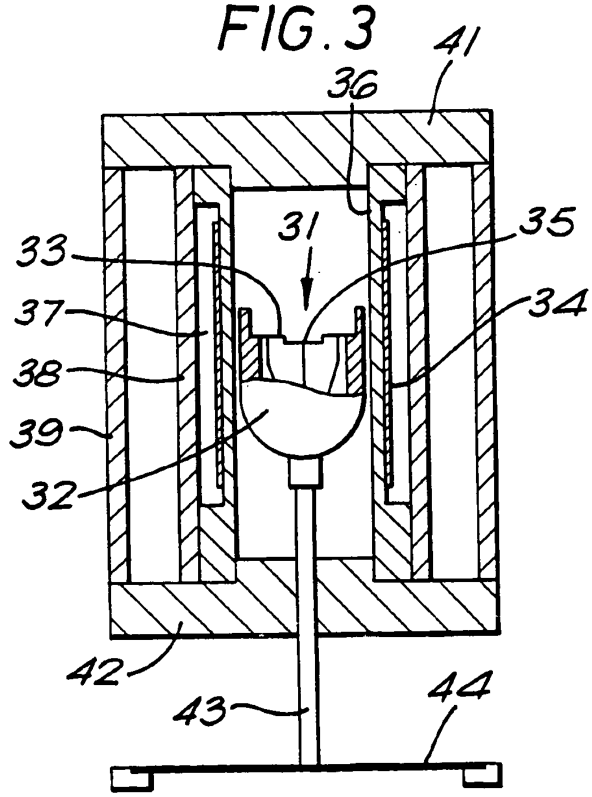


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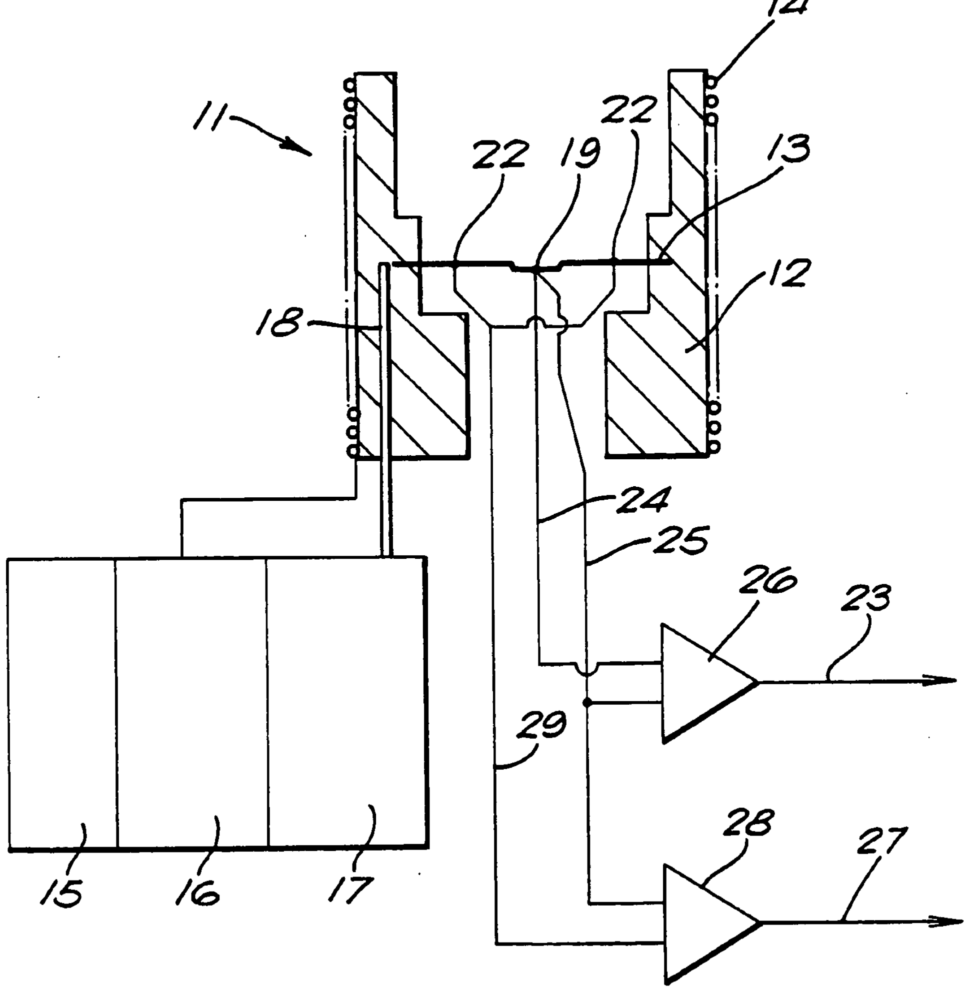
FIG. 2

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International Application No
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**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 5 G01N25/48

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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| Y | LU,A,46 246 (CEA) 4 June 1964<br>see page 3, line 24 - page 4, line 25; figures 1-3<br>--- | 1 |
| Y | US,A,4 126 032 (M. IKEDA) 21 November 1977<br>see abstract; figure 1<br>--- | 1 |
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| A | PATENT ABSTRACTS OF JAPAN<br>vol. 7, no. 32 (P-174)(1177) 8 February 1983<br>& JP,A,57 186 147 (K. GIJUTSUIN) 16 November 1982<br>see abstract<br>---<br>-/-- | 1 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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